

**This Page Is Inserted by IFW Operations  
and is not a part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

# PATENT SPECIFICATION

DRAWINGS ATTACHED

913,289



Date of Application and filing Complete Specification March 30, 1960.

No. 11182/60.

Application made In United States of America (Nos. 809032, 809160, 809161 and 809162) on April 27, 1959.

Complete Specification Published Dec. 19, 1962.

Index at acceptance:—Class 140, A2N(1:3), A5G(7:9), A10B(1:3).

International Classification:—B29d.

## COMPLETE SPECIFICATION

### Process for the Production of Laminated Structures and particularly Laminated Films and Foils

We, THE DOW CHEMICAL COMPANY, a Corporation organized and existing under the Laws of the State of Delaware, United States of America, of Midland, County of Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved process for the production of laminates from thermoplastic polymers and particularly of laminated or composite film structures.

Films and other shaped articles of polyethylene, polypropylene and the like non-aromatic hydrocarbon olefin polymers have many attractive characteristics including, in general: pronounced chemical inertness; good physical properties (especially significant strength, toughness and resistance to tearing); excellent behaviour, without marked tendency to embrittlement, at low temperatures; satisfactory moisture vapour barrier properties; and, in particular, unusual capability for and easy susceptibility of being heat sealed in order to form and provide strong, permanent joints upon being thermally welded or fused together when in contact under the influence of heat at elevated temperatures and, if desired, pressure along the seam or other welded area being joined.

The latter feature is of great desirability and decided advantage for fabrication of film and analogous sheet-like structures into many useful articles and products (such as bags, pouches, etc.) and in the general utilization thereof for many wrapping and packaging applications.

On the other hand, film structures and the like shaped articles of some of the thermoplastic materials such as polyesters, cellulose

esters, vinylidene copolymer coated polyolefines, and vinylidene copolymer coated regenerated cellulose, are, generally to a certain extent thermally insensitive materials that do not generate any seal strength upon being attempted to be heat sealed or thermally welded together. These and other thermoplastic polymers, besides having generally good properties and characteristics as film materials, have an unusual ability to provide particularly effective barriers against the transmission or permeation of gases and vapours in addition to water vapour. Furthermore, many of these thermoplastic films are usually not as prone to becoming surface scuffed or marred in use as are the typical polymers of ethylene, propylene and the like.

Polyethylene and the like film and other articles is well known, commonly have a smooth and sleek, relatively slippery and wax like surface which is poorly adapted to provide for suitable adhesion or anchorage of applied materials by mere physical attachment. In addition, the relatively inert chemical nature of polyethylene and the like non-aromatic hydrocarbon polyolefins resist the efficient attachment of most materials by chemical inter-linkage or bonding. This makes it very difficult, if not impossible, to join to the surface of most thermoplastic films or similar structures, films of polyethylene and the like non-aromatic hydrocarbon polymers. In an attempt to overcome these difficulties, it has been proposed to employ certain compounds, among them polyalkylene imines, as adhesion-promoting intermediary layers. In this manner, composite film structures and joints of various thermoplastic polymers with polyethylene polymers can be produced.

The process of the present invention permits the production of laminated structures and particularly laminated multi-layer films

[Price

having considerably improved properties. Unexpected high adhesion strength can be achieved by the present invention which provides a process for the production of laminated structures which consist of or contain a thermoplastic polymeric substrate to at least one side of which is intimately joined a layer of a non-aromatic hydrocarbon polymer over a thin adhesion-promoting intermediary layer of a polyalkylene imine, in which process the polyolefin is deposited onto the polyalkylene imine modified surface of the preformed thermoplastic polymeric substrate in form of an extruded molten layer or film.

Advantageously the non-aromatic hydrocarbon polymer is polyethylene or polypropylene.

The improved process of the present invention can be employed with particular advantage where the substrate is a film, foil, sheet or similarly shaped structure of a polyester, particularly of polyethylene terephthalate, a cellulose ester, especially of cellulose acetate or cellulose propionate, a regenerated cellulose or a non-aromatic polyolefin such as polyethylene or polypropylene which regenerated cellulose or polyolefin have a vinylidene chloride copolymer coating on the side to be joined with the polyolefin by the process of the present invention. Satisfactory results are generally obtained if one employs 5 grams to 95 grams, and preferably between 20 and 50 grams of the polyalkylene imine per 100 square meters of the thermoplastic substrate. It is generally preferred to employ relatively low molecular weight polyalkylene imines which are water soluble.

The novel method of the present invention permits efficient and effective coating or lamination of films, foils, or analogous sheet-like substrates of film forming thermoplastic polymeric materials with tightly adhering integral layers of non-aromatic hydrocarbon olefin polymers. The composite structures or articles, and particularly the films, obtained in the process of the present invention are particularly adapted for the employment as flexible vapourproof materials which are capable of being joined or thermally welded by conventional heat-sealing techniques for packaging and the like protective and decorative uses.

In the preferred method of the present invention, film, foil and analogous sheet-like substrates of film-forming thermoplastic polymeric materials, particularly of polyethylene terephthalate, cellulose acetate, vinylidene chloride copolymer coated film-forming polyethylene or polypropylene resin, or vinylidene chloride copolymer coated regenerated cellulose are effectively provided with a tightly adhered and firmly anchored coating or sheet-like layer of laminated polyethylene or the like non-aromatic hydrocarbon olefin polymer

(including, as has been indicated, polypropylene, polybutylene, copolymers of ethylene and propylene, etc.) by a method which comprises initially applying to the surface of the polymer substrate (or treating such surfaces with) a small quantity of a polyalkylene imine compound as an intermediate adhesion-promoting coat or layer; and subsequently applying over the polyalkylene imine treated surface of the polyester substrate a fused or molten sheet-like coating layer of the desired polyolefin polymer; then cooling and solidifying the deposited polyolefin layer on the polyalkylene imine treated surface of the polyester substrate.

The resulting composite or laminated film or foil structures or articles which may advantageously be obtained by practice of the present invention possess, to an unusual degree, practically all of the desirable and beneficial attributes and properties of both the polymer substrate layer and the applied polyolefin layer that are laminated thereon.

In the accompanying drawings, Figure 1 perspectively depicts a composite or laminate film or foil structure in accordance with the invention; Figure 2 illustrates the laminate structure of Figure 1 in fragmentary cross-section; Figure 3, in schematic and diagrammatic elevation, partly in cross-section, illustrates one means of preparing the laminated film products of the invention; Figure 4 shows a means of pre-applying the intermediate polyalkylene imine adhesion promoting coating to the polyester substrate in order to provide pre-treated stock satisfactory for subsequent manufacture of the desired laminated, sheet-like products; and Figure 5, represented in a manner analogous to that of Figures 3 and 4, schematically more particularly demonstrates the application of the polyolefin layer to the treated substrate.

With initial reference to Figures 1 and 2, there are illustrated the laminated film or foil products of the present invention, generally designated by the reference numeral 10. The composite film 10 is comprised of a base polymeric film or sheet layer 11 (substrate) over which there is deposited an intermediate adhesion-promoting coat or layer 13 of a small quantity of polyalkylene imine that is applied in a uniform or substantially uniform and relatively thin formation, to and with which there is effectively and efficiently laminated or bonded a coated layer 14 of the polyolefin polymer.

As mentioned, the composite, laminated film product 10 retains the essential and advantageous properties of both of the resin layers in the bonded integral structure. It is strong, tough and tear-resistant and has an attractive and highly decorative appearance. Depending on the nature of the polymer employed as the base or substrate its surface tends to be more scuff-resistant and harder-

to-mat than plain polyethylene and the like non-aromatic hydrocarbon polymers. In addition, the laminated film product generally remains strong and flexible at relatively low temperatures and, of great significance, is in many instances impermeable to most gases and vapours, being a particularly effective moisture barrier.

In the case of the vinylidene chloride coated polyolefines, laminated in accordance with the present invention with another layer of a non-aromatic hydrocarbon polymer layer, the composite or laminated structure is strong, tough and tear-resistant and has an attractive and highly decorative appearance. The laminated film product generally remains strong and flexible at relatively low temperatures and, of great significance, is extremely impermeable to most gases and vapours, being a particularly effective moisture barrier.

The composite film or sheet-like products of the present invention are possessed of a strong and effective bond between the laminated substrate and polyolefin layers 11 and 14, respectively. In most instances, the joined layers are extremely difficult, if not impossible, to strip apart or delaminate by ordinary physical methods.

The composite film and analogous sheet-like structures of the present invention have particularly utility as wrapping and packaging materials for foodstuffs (as in the preparation of gas flush packages for cheeses and so forth) and for other articles such as pharmaceuticals, medicinal products, hardware, etc., especially in instances when it is desired to protect the package article from unwanted change in moisture content. The film products are also advantageous for wrapping and packaging foodstuffs and other materials which are intended to be handled or maintained and stored at relatively low temperatures in a refrigerated, or even in a frozen, condition. Besides providing protection as a strong and tough flexible covering, they also more effectively prevent dehydration of the packaged articles and, where required, tend to avoid development of the condition known as "freezer burn" which frequently occurs in inadequately protected frozen foods.

In addition, the laminated structures which have a layer of polyolefin laminated onto the vinylidene chloride coated polyolefin base may be utilized with great advantage for such applications as vacuum forming and where deep drawing requirements are critical in moulding and forming operations using preformed polyolefin sheet. These composite structures retain superior appearances and finishes during drawing operations as compared to ordinary polyvinylidene chloride copolymer coated polyethylene and the like polyolefin film and sheets. When they are utilized for such purposes, they tend to most advantageously overcome and minimize the

difficulties encountered by possible cracking, separation and tearing or other deformation of the interlaminated vinylidene chloride copolymer coating during the deep drawing operation.

Although the advantageous composite articles resulting from practice of the present invention are herein predominantly illustrated and described as film, foil and similar sheet-like products that are particularly useful for bags and the like heat-sealable packages, it is readily apparent that in many instances other composite structures and articles may also be prepared and provided such as and including tubes, flexible bottles, cartons, boxes and other containers, and liners therefor, and so forth.

Advantageously, the polymeric substrate film 11 which is laminated with the applied polyolefin layer is a relatively thin film or sheet-like structure. Likewise, the laminated layer 14 of the polyolefin resin that is bonded to the polymeric substrate by the intermediate polyalkylene imine adhesion-promoting coating 13 on the surface of the polymeric substrate is a relatively thin deposit. In this way, there is provided an ultimate laminated film product 10 of correspondingly relatively little thickness.

Beneficial results, for example, are readily obtainable when the substrate film 11 has a thickness of at least about 6 microns and not greatly in excess of about 250 microns. It is frequently desirable for the preformed substrate film structure to have a thickness between about 12.5 microns and 50 to 65 microns. The vinylidene chloride copolymer coating on the preformed polyolefin substrate generally has a thickness of at least about 0.5 micron, preferably between about 2.5 and 50 microns and, usually, less than about 12.5 microns.

Most commercial cellulose acetate film, for example, has a thickness of from about 20 to 25 microns.

Likewise, it is generally advantageous for the laminated polyolefin layer to have a thickness between about 6.3 microns and about 255 microns and may frequently be more advantageous for the thickness of the applied polyolefin layer to be between about 25 and 50 microns. Thus, the total thickness of the composite film product may advantageously be between about 12.7 microns and about 500 microns and, frequently more advantageously between about 38 and 100 microns.

The film-forming, resinous polyester polymer substrates that are contemplated as being adapted for employment in the practice of the present invention include any of the polyester high polymers of the type that are well known in the art and which are capable of being fabricated into useful film and related structures. Such film-forming polyester polymers are the essentially linear condensation pro-

ducts of glycols and polyglycols with dicarboxylic organic acids, which acids are ordinarily aromatic in nature, as, for example, dicarboxylic benzene and substituted benzene acids. In particular, the polyester polymers utilized in the film substrates employed in the practice of the present invention may be identical with or similar and analogous to the highly polymeric linear terephthalic esters which have been described, in United States Patent Specification No. 2,465,319. Specifically, there may be mentioned as a specially desirable species of such material the polyester polymers of terephthalic acid and propylene or ethylene glycol, or their mixtures.

The film-forming resinous cellulose ester substrates that are contemplated as being adapted for employment in the practice of the present invention include any of the commonly available types of cellulose acetate and other cellulose esters of the film-forming variety, such as cellulose propionate, cellulose butyrate and the like and mixtures thereof that are frequently utilized for the preparation of useful film, foil, sheet and related structures. As indicated, an especially desirable species of such material is cellulose acetate. Advantageously, the cellulose ester substrates can be used directly in the film, foil and other sheet-like form in which they are ordinarily obtained, in which form they may contain suitable plasticizers, stabilizing agents and other beneficial agents of the frequently employed variety.

The vinylidene chloride copolymer coated regenerated cellulose substrates that are contemplated as being adapted for employment in the practice of the present invention include any of the regenerated cellulose materials of the type that are well-known in the art which are capable of being fabricated into useful film and related structures and coated on one or both surfaces with a layer of vinylidene chloride copolymer.

The regenerated cellulose film or foil of greatest interest is that which, as indicated, is frequently characterized as being cellophane and which is obtained from viscose by the well-known viscose process. This involves regeneration or coagulation of viscose in a suitable acid or other coagulating bath; followed by one or more of such operations on the thereby obtained article as washing, desulfurizing, bleaching, washing, drying, etc. If desired, however, the regenerated cellulose films or foils that is coated and utilized for the present invention may be obtained by practice of the well-known cuprammonium process.

The polyvinylidene coating on the surface of the coated regenerated cellulose film or of the coated substrate polyolefin polymer film may advantageously be a copolymer of vinylidene chloride and vinyl chloride; or a copolymer of vinylidene chloride and acryloni-

trile; or a copolymer of vinylidene chloride and acrylic acid or its ester derivatives. It is particularly advantageous for the coating on the regenerated cellulose film to consist of a crystalline vinylidene copolymer and even more advantageous for such coatings to consist of copolymer of vinyl chloride and vinylidene chloride that contain at least about 80 weight per cent of polymerized vinylidene chloride in the copolymer molecule or, if desired, such copolymers of vinylidene chloride and acrylonitrile that contain at least about 60 and, preferably, from 85 to 95 weight per cent of vinylidene chloride in the copolymer molecule. Of course, other copolymers of vinylidene chloride may also be employed, particularly those comprised of at least about 25 weight per cent of polymerized vinylidene chloride in the copolymer molecule with any balance being one or more other ethylenically unsaturated monomers that are copolymerizable with vinylidene chloride.

In this connection, the polyolefin polymer in the vinylidene coated copolymer preformed substrate layer 11 and that in the applied layer 14 may either be the same, or diverse, polyolefins within the hereinafter indicated scope, as may be desired in particular instances and to meet the requirements for given applications. Thus, both the substrate and the applied layers may be polyethylene. Or they both may be polypropylene, and so forth. Conversely, if desired, the substrate may be polyethylene and the applied layer supported thereon polypropylene, or vice-versa, and so forth.

The vinylidene copolymer layer on the surface of the polyolefin polymer may be provided in any suitable way. Thus, it may be deposited over the surface of the polyolefin substrate after the substrate has been surface chlorinated to improve the adhesion thereon of applied polymer coatings. Such surface chlorination may advantageously be about to the same extent as is necessary to promote the adhesion of printing inks and the like on the polyolefin polymer film. Or, the surface may be improved for retention of applied vinylidene copolymer coatings by treatment with aqueous quench baths of various hydrohalic (such as hydrochloric) acids; nitric acid; sulfuric acid; cleaning solution, and so forth, all in the known manner. Alternatively, the vinylidene chloride copolymer coating may be effectively bonded to the surface of the polyolefin substrate by applying the copolymer from a latex emulsion composition thereof containing various surface active adhesion promoting agents which effect and secure the desired tight lamination of the vinylidene chloride copolymer resin to the polyolefin substrate. In still another way, the polyolefin polymer substrate may be provided with the vinylidene chloride copolymer coating by

applying the latter, from any desired coating compositions, to the surface of a polyolefin polymer that has been pre-treated by exposure to substantial dosages of high energy radiation, as from a Van de Graff generator or from various radioactive sources, in a field of at least about 40000 roentgens per hour intensity and, generally, much greater.

Advantageously, and frequently with optimum results, the substrates of polyethylene and the like non-aromatic hydrocarbon polymers, may be effectively provided with a tightly-adhering and firmly anchored coating of a vinylidene chloride polymer resin by a method which comprises first activating the surface of the polyolefin polymer substrate, as by means of flame contact or electron bombardment or electric treatment, so as to induce substantial chemical unsaturation and physicochemical change on the surface; then treating the activated surface with a small quantity of a polyalkylene imine compound; and subsequently applying a layer of a vinylidene chloride polymer resin over the activated and polyalkylene imine treated surface. This method has been described in and is among the subjects of copending Application No. 10675/60.

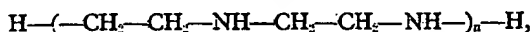
The same polyalkylene imines as used in the practice of the present invention for promoting adhesion in the lamination of the applied polyolefin layer over the vinylidene chloride copolymer coated polyolefin or other thermoplastic substrate may be employed with great advantage over the activated surface of the polyolefin in the substrate to achieve good and efficient bonding of the vinylidene chloride copolymer coated layer thereon. In this connection, the polyalkylene imine may be employed and applied in about the same way, using about the same conditions and techniques, for bonding the layer of vinylidene chloride copolymer to the surface of an activated polyolefin polymer film as is hereinafter more fully described in respect of application of the polyalkylene imine over the vinylidene chloride copolymer coated layer of the polyolefin substrate to facilitate lamination of the applied polyolefin layer therewith.

The polyethylene or other non-aromatic hydrocarbon polyolefin which is employed in the practice of the present invention may be polymers of any normally solid and film-forming nature. For example, the polymers of ethylene which are employed may be those, or similar to those, which sometimes are re-

ferred to as "polythenes" and which may be obtained by polymerizing ethylene in a basic aqueous medium and in the presence of polymerization-favouring quantities of oxygen under relatively high pressures in excess of 500 or 1000 atmospheres at temperatures which may be between 150 and 275° C. Or, if desired, the ethylene and other non-aromatic hydrocarbon olefin polymers may be essentially linear and unbranched polymers, or polyolefin products similar to these materials. The essentially linear and unbranched, macromolecular, high density polyethylenes have been referred to as "ultrathenes". They ordinarily have greater apparent molecular weights (as may be determined from such characteristics as their melt viscosities and the like) than the "polythene" type polyethylenes which are usually in excess of at least about 20000 and generally in excess of about 40000; densities of about 0.94—0.96 gram per cubic centimeter; and melting points in the neighbourhood of 125—135° C. They are also ordinarily found to have a more crystalline nature than conventional polyethylenes and may contain less than 3.0 and even less than 0.3 methyl radicals per 100 methylene groups in the polymer molecule. The essentially linear and unbranched polymers of ethylene and other non-aromatic hydrocarbon olefins may be obtained under relatively low pressures of 1 to 100 atmospheres using such catalysts for polymerizing the ethylene or other olefin as mixtures of strong reducing agents and compounds of Group IV-B, V-B and VI-B metals of the Periodic System; chromium oxide on silicated alumina; hexavalent molybdenum compounds; and charcoal supported nickel-cobalt.

As is apparent, the polyolefin polymers utilized in the practice of the present invention are generally prepared by polymerization of monoolefinic aliphatic olefin monomers, such as ethylene, propylene, butylene and so forth (including polymerizable mixtures thereof) that contain from 2 to about 8 carbon atoms, which monomeric olefins are frequently known as being 1-olefins due to their characteristic terminally unsaturated structures.

The polyalkylene imines which are utilized for providing the intermediate adhesion promoting coating deposit 13 in the composite film structures of the invention to secure the desired effective lamination between the polymeric substrate and polyolefin layers 11 and 14 are advantageously one of the polyethylene imines which are of the general structure:—



in which  $n$  has a numerical value of at least 1 and may be a larger, plural integer having a value as great as 1000—2000 and more. Thus, when a polyethylene imine is utilized for treating the surface of the substrate, it may be of any desired molecular weight in

which the material can be obtained. It is generally most advantageous, however, to avoid use of very low molecular weight materials having excessive volatilities.

As is apparent, other polyalkylene imines equivalent to polyethylene imines (obtained

by polymerization, in the known way, of the corresponding alkylene imines) may also be utilized as an intermediate adhesion-promoting coat to treat the surface of the substrate layer in place of, or in combination with, the polyethylene imine. Ordinarily, it is of greatest practical significance for these to include any of the homologous polyalkylene imines which are comprised of alkylene units of less than about 4 carbon atoms. In most cases, although no limiting implications are intended, the polyalkylene imines of greatest interest to employ are the relatively low polymer, water-soluble materials whose viscosity in 20 per cent aqueous solution at 20° C. are on the order of 100 poises.

Only a very small quantity of the polyalkylene imine need be deposited as an intermediate adhesion promoting coating on the surface of the polymeric substrate film to which the polyethylene or other non-aromatic hydrocarbon polymer layer is laminated. In general, an amount between about 5 grams and 95 grams per one hundred square meters of substrate surface are suitable to facilitate and promote the adhesion of the polyolefin polymer layer on the substrate surface being laminated. Frequently, between about 20 and 50 grams per one hundred square meter provides an entirely satisfactory result.

Although it can be directly applied if desired, the deposition of the polyalkylene imine is generally better and more conventionally and easily accomplished from a solution or dispersion of the adhesion-promoting agent in a suitable solvent, such as acetone, methyl ethyl ketone, methyl isopropyl ketone, lower alkyl alcohols (particularly those of less than 4 carbon atoms), etc. Methanol, ethanol and isopropanol are oftentimes found to provide optimum solvent behavior for the polyalkylene imine. Advantageously, a relatively dilute solution of the polyalkylene imine treating agent in the solvent is employed, such as one having a concentration of the polyalkylene imine between about 0.01 and 2 per cent. Frequently, it is even more beneficial for the applying solution of the polyalkylene imine to contain between about 1/8 and 1/2 per cent by weight of the dissolved adhesion promoting agent. This facilitates the uniform and general deposition over the surface of the substrate of the relatively minute quantities of polyalkylene imine needed for the intermediate adhesion-promoting coating on the polymeric substrate prior to deposit or placement of the polyolefin polymer layer being laminated.

When the polyalkylene imines (such as polyethylene imine) are employed in too great a concentration on the substrate surface, they tend to result in undesirably weak and unsatisfactory laminated structures.

The coating application of the polyalkylene imine anchor layer may be made by spray-

ing or spread coating the solution thereof on the surface of the polymeric substrate being laminated to the polyolefin layer. Necessarily, the coating of the strongly cationic polyalkylene imine agent is dried by air or by means of heat at an elevated temperature on the surface of the polymeric substrate prior to actual application thereover of the polyolefin layer being laminated therein.

In this connection, it is generally desirable to employ a relatively fugacious solvent in order to allow rapid and ready drying (with minimized or no external application of heat) of the applied polyalkylene imine solution. Thus, isopropanol, ethanol, or methanol are, as has been indicated, most beneficial to employ as solvents for the applying solution of the polyalkylene imine. Such solvents can be easily dried in cool air (such as air at room temperature or with minimum requirements for heat) to deposit the adhesion-promoting intermediate layer of the polyalkylene imine on the surface of the substrate. Frequently, however, the use of warm air is found to be more practical for drying, especially when conditions of relatively high humidity in the atmosphere are encountered.

With reference to Figure 3 of the drawing, there is illustrated one means of manufacturing the composite film products of the present invention. As shown, the substrate 11 is passed from any suitable source of supply (not shown) under a point at which the polyalkylene imine is applied to its surface. This may be accomplished, as illustrated, by a spray 19 of a suitable applying solution or other composition of the polyalkylene imine which is directed from a nozzle 18 controlled by a valve 17 to handle the polyalkylene imine solution in the conduit 16 from any suitable source of supply (not shown).

After application on the surface of the substrate 11, the polyalkylene imine-treated material is passed through a drying oven, illustrated schematically by the reference numeral 22, which heats the applied material sufficiently to remove all solvent vehicle therefrom prior to lamination of the polyolefin layer to the polyalkylene imine-treated substrate surface. While the drying oven 22 may generate any suitable temperature adequate to vaporize the solvent vehicle from the polyalkylene imine (but lower than that which might degrade the applied material or the substrate), it is generally advantageous to operate the oven in the neighborhood of 65° C. when the solvent vehicles of usual interest are employed in the polyalkylene imine solution. In this connection, as has been indicated, it is necessary to dry the polyalkylene imine adhesion-promoting layer completely from any associated solvent vehicle before passing the pre-treated substrate, indicated generally by reference numeral 12, to the subsequent polyolefin laminating operation.

After being dried on the surface of the substrate, the polyalkylene imine-treated material 12 is laminated with the desired polyolefin layer 14. This may be accomplished by passing the preheated substrate 12 between the nip of a pair of cooperating rolls consisting of a back-up roll 24 and a chill roll 25, driven by any suitable means and operating in the directions indicated by the arrows, wherein the molten polyolefin layer is applied to the pretreated substrate 12 and chilled and efficiently laminated to form the composite film.

Thus, the polyolefin may be contained in an extruder 27, of any conventional or desired construction, adapted to expel a falling sheet-like layer or curtain 30 of molten polyolefin through a suitable die orifice 28 onto the polyalkylene imine-containing surface of the pretreated substrate 12 in the nip of the rolls 24 and 25. It is generally advantageous to maintain the polyolefin in the extruder, particularly when it is polyethylene, at a temperature sufficiently high to ensure its remaining in a fused and molten condition after being passed from the die to fall through the air as a layer on the surface of the pretreated film. Thus, it is generally desirable for the extruded polymer to make contact with the pretreated substrate while it is at a temperature of at least about 175° to 190° C. (at actual contact or juncture with the pretreated substrate), particularly in the instances when polyethylene is being laminated. This generally requires the molten polymer in the extruder barrel, as it leaves the die lips, to be at a temperature between about 285° and 315° C.

In this connection, although the molten polyolefin may be passed any distance through the atmosphere from the outlet of the die 28 to the point of juncture with the pretreated substrate, it is generally advantageous for a distance of not more than about 30 cm, advantageously about 15 to 25 cm, to be utilized.

Immediately upon being applied, the polyolefin layer from the molten sheet 30 is chilled, solidified and laminated in place by the action of the chill rod 25 which is maintained at a temperature above the sticking temperature of the polyolefin but below its fusion point, which temperature, frequently, is most advantageously maintained in the range from about 26° to 38° C.

After being laminated in place, the polyolefin layer 14 on the treated substrate 12 provides the composite film product 10 of the present invention. The composite product may be taken up for subsequent use by any suitable means or in any desired manner, such as by take-up roll 31 onto which the composite film is shown being wound in Figure 3 of the drawing. Of course, if desired, it can be directly passed, without intermediate

take-up, to any subsequent manufacturing operation in which it may be employed.

As a matter of actual practice, it is generally advantageous to form the pretreated substrate in the manner illustrated in Figure 4 of the drawing. This provides for a supply of the intermediate treated substrate for subsequent lamination of such material. As shown in Figure 4, the adhesion-promoting polyalkylene imine coating 13 is provided and dried in place by spread coating the applying solution thereof on the substrate 11 to form the intermediate, polyalkylene imine-treated substrate material 12. Thus, instead of spraying the applying solution of the polyalkylene imine onto the surface of the substrate 11, it may advantageously be applied from a gravure coating roll and dried prior to take up as an intermediate product.

As is specifically illustrated in Figure 4, a supply of the substrate 11 in roll 32 is unwound and passed between a pair of cooperating rollers consisting of a gravure roll 36 (which advantageously may be knurled) and an upper impression roll 39 (which advantageously may have a rubber or the like surface). The gravure roll 36 is immersed in a suitable supply 34 of applying solution of the polyalkylene imine contained in a gravure tank or the like container 33. The gravure roll 36, operating in the direction indicated by the arrow, picks up the applying solution 34 of the polyalkylene imine and applies it to the surface of the substrate 11 being treated. Excess applying solution may advantageously be wiped from the surface of the gravure roll 36 by a doctor knife 37 or the like scraper to ensure uniform application and avoid excesses of the solution. The treated substrate material is then passed around a roll 40 through a dryer 44 wherein the solvent vehicle is removed from the polyalkylene imine to provide the pretreated substrate intermediate 12. The intermediate product 12, advantageously, may then be taken into a supply roll 44 as stock material for subsequent use in the laminating operation.

Great care should be taken in applying the molten polyolefin to the surface of the pretreated substrate. It is essential that the sheet of fused polymer to be laminated into the composite film product is not allowed to become solidified before contacting the treated substrate, as by first falling on the chill roll before entering the nip of the rolls wherein the lamination is effected. It is generally desirable, as illustrated in Figure 5 of the drawing, to feed the molten polyolefin polymer 30 on to the surface of the pretreated substrate 12 just before the material to be laminated is passed through the nip of the cooperating rollers 24-25.

Actually, better results are generally obtained when the molten polyolefin 30 makes initial contact or juncture with the substrate



prior to being chilled at just about the nip of the rolls, although suitable results are obtained if contact is made some distance back before the nip. Generally, however, the actual lateral distance at which contact is made before entering the nip of the rolls 24—25 (as illustrated by the dimension "x" in Figure 5) should be within several centimeters and advantageously with about 2.5 cm from the nip of the roll.

#### EXAMPLE 1

A 12.7 micron polyethylene terephthalate film was surface-treated with polyethylene imine at the rate of about 7.5 l. of applying solution per 1000 square meters of film using an applying solution consisting of about 3/8 per cent by weight, based on the weight of the applying solution, of polyethylene imine in ethanol. The polyethylene imine employed had an average molecular weight on the order of about 7090. The applying solution was prepared by mixing the alcohol with 3/4 per cent by weight of a 50 per cent aqueous solution of the polyethylene imine.

The application of the polyethylene imine solution was made in a manner similar to that illustrated in Figure 4 of the drawing, using gravure rolls having a diameter of about 15.2 cm and a width of about 102 cm for application of the solution to the film substrate. After application of the polyethylene imine, the adhesion-promoting coating thereof was dried on the surface of the substrate in an oven at a temperature of about 65° C. prior to being taken up as a stock or supply roll of the intermediate pretreated substrate film.

The thereby obtained pretreated substrate was then laminated with polyethylene using a procedure as illustrated in Figure 5 of the drawing. The polyethylene imine coated substrate film was run at a linear rate of about 30 meters per minute under an extruder for the polyethylene discharging into the nip of a pair of rolls, consisting of a 45.7 cm diameter back-up roll and a 60 cm diameter chill roll (with the chill roll being maintained at about 27° C.), through which the substrate was being passed.

About a 50 micron layer of polyethylene was applied from the extruder to the pretreated substrate by feeding the molten polymer layer in the form of a falling sheet or curtain (through about 20 cm fall) from the die lips to the nip of the rolls. The temperature of the polyethylene in the barrel of the extruder at the die was about 315° C. Its temperature at contact with the substrate was about 190° C.

The polyethylene employed was the conventional, branch-structured variety of polyethylene (of the "polythene" type) having a melt index (according to ASTM D-1238—52T) of about 3.0. After being cooled and solidified and laminated in place, the resulting

composite film structure was taken up into a supply roll.

The resulting composite film structure was tested to determine the cohesive properties of the laminated layers in the film and the best sealability of the product by means of a heat seal peel test. This test consisted of measuring the force in kg that was necessary to separate 2.54 cm wide strips of the applied polyethylene layers which had been heat sealed together at 149° C. and pulled in a Scott Tester in the machine direction. The composite film did not fail in any instance, either as regards the laminated layers or the heat sealed strips, when less than 1.36 kg of pull was exerted on any of the sealed specimens tested.

#### EXAMPLE 2

About the same results are obtained when the procedure of Example 1 is repeated excepting to laminate essentially linear and unbranched polyethylene in the composite film structure being made; or to apply a layer of polyethylene or a layer of a copolymer of polypropylene and ethylene (such as one containing about equal weight percentages of each monomer in the polyolefin product) on the treated substrate; or when other film-forming polyester substrates are utilized; or when other polyalkylene imines within the scope indicated in the foregoing specification are employed to provide the adhesion promoting coating on the surface of the substrate with which the polyolefin layer is laminated.

#### EXAMPLE 3

A 22 microns thick cellulose acetate film was surface-treated with polyethylene imine as described in Example 1. The thereby-obtained pretreated substrate was then laminated with polyethylene using a procedure as illustrated in Example 1. The polyethylene imine coated substrate film was run at a linear rate of about 30 meters per minute and about a 50 micron layer of polyethylene was applied from the extruder to the pretreated substrate.

The polyethylene employed was the conventional, branch-structured variety of polyethylene (of the "polythene" type) having a melt index (according to ASTM D-1238—52T) of about 3.0. After being cooled and solidified and laminated in place, the resulting composite film structure was taken up into a supply roll. The resulting composite film structure was tested to determine the cohesive properties of the laminated layers in the film and the heat sealability of the product by means of a heat seal peel test, as described in Example 1. The composite film did not fail in any instance either as regards the laminated layers or the heat sealed strips, when less than 1.36 kg of pull were exerted on any of the sealed specimens tested.

## EXAMPLE 4

About the same results are obtained when the foregoing procedure of Example 3 is repeated excepting to laminate essentially linear and unbranched polyethylene in the composite film structure being made; or to apply a layer of polyethylene or a layer of a copolymer of polypropylene and ethylene (such as one containing about equal weight percentages of each monomer in the polyolefin products) on the treated substrate; or when other film-forming cellulose ester substrates are utilized, such as cellulose propionate and cellulose butyrate; or when other polyalkylene amines within the scope indicated in the foregoing specification are employed to provide the adhesion-promoting coating on the surface of the substrate with which the polyolefin layer is laminated.

## EXAMPLE 5

A film of regenerated cellulose (from viscosim 6'ZZ inoqe jo ssaxpiti e 3uiaeq (3soo and coated on one side with about a 2.5 micron deposit of a copolymer of about 85 weight per cent of vinylidene chloride and 15 weight per cent of vinyl chloride was treated on its coated surface with polyethylene imine at the rate and in the manner described in Example 1.

The thereby-obtained pre-treated substrate was then laminated with polyethylene using a procedure as described in Example 1. The polyethylene imine coated substrate film was run at a linear rate of about 30 meters per minute and about a 50 microns layer of polyethylene was applied from the extruder to the pre-treated substrate.

The polyethylene employed was the conventional branch-structured variety of polyethylene (of the "polythene" type) having a melt index (according to ASTM D-1238—52T) of about 3.0. After being cooled and solidified and laminated in place, the resulting composite film structures were taken up into a supply roll.

The resulting composite film structures were tested to determine the cohesive properties of the laminated layers in the film and the heat sealability of the product by means of a heat seal peel test as described in Example 1. The composite film did not fail in any instance, either as regards the laminated layers or the heat sealed strips, when less than 1.36 kg of pull were exerted on any of the sealed specimens tested.

## EXAMPLE 6

About the same results are obtained when the procedure of Example 5 is repeated excepting to laminate essentially linear and unbranched polyethylene in the composite film structure being made; or to apply a layer of polyethylene or a layer of a copolymer of polypropylene and ethylene (such as one con-

taining about equal weight percentages of each monomer in the polyolefin product) on the treated substrate; or when other vinylidene chloride copolymer coated regenerated cellulose substrates are utilized including those made from other varieties of regenerated cellulose and those having other specific types of vinylidene chloride copolymer coatings thereon; or when other polyalkylene imines within the scope indicated in the foregoing specification are employed to provide the adhesion-promoting coating on the surface of the substrate with which the polyolefin layer is laminated.

## EXAMPLE 7

A 25.4 micron polyethylene film of the conventional branch structured "polythene" type having a melt index of about 3.0 (according to ASTM D-1238—52T) and having a vinylidene chloride copolymer coating of about 2.5 microns on one side was treated on its coated surface with polyethylene imine at the rate and in the manner described in Example 1.

The vinylidene chloride copolymer coated polyethylene substrate was prepared by application of the vinylidene chloride copolymer resin from about a 20 per cent lacquer solution in acetone over the surface of polyethylene which had been flame treated for activation then pretreated with polyethylene imine prior to deposition of the coating thereover. The film was flame treated to activate its surface and alter the physiochemical properties thereof in the known manner in the oxidizing portion of a flame using natural gas as the fuel. After being activated by the flame-contact treatment, the film was treated with polyethylene imine having an average molecular weight on the order of about 7000. The polyethylene imine was machine coated over the films using a concentration of about 0.25 per cent of the polyethylene imine dissolved in acetone. After application of the polyethylene imine, the anchor coating was dried. This was followed by application of the vinylidene chloride copolymer thereover from the lacquer solution of the copolymer, which was cast on the film to provide a uniform coating after removal of solvent being dried. The vinylidene chloride copolymer that was actually utilized in the coating was a copolymer of vinylidene chloride and acrylonitrile containing the interpolymerized monomers in about an 80:20 per cent by weight basis, respectively.

The application of the adhesion promoting polyethylene imine solution over the coater surface of the polyethylene substrate was made in a manner similar to that described in Example 1.

The thereby-obtained pretreated vinylidene chloride copolymer coated substrate was then laminated with another polyethylene

layer using a procedure as described in Example 1.

About a 50 micron layer of supported polyethylene was applied from the extruder to the pretreated preformed supporting substrate.

The polyethylene employed in the supporting applied layer was also the conventional, branch-structured variety of polyethylene (of the "polythene" type). Its melt index was also about 3.0. After being cooled and solidified and laminated in place, the resulting composite film structure was taken up into a supply roll.

The resulting composite film structure was tested to determine the cohesive properties of the laminated layers in the film and the heat sealability of the product by means of a heat seal peel test, as described in Example 1.

#### EXAMPLE 8

About the same results are obtained when the procedure of Example 7 is repeated excepting to laminate essentially linear and unbranched polyethylene supported layers in the composite film structure being made; or to apply a layer of polyethylene or a layer of a copolymer of polypropylene and ethylene (such as one containing about equal weight percentages of each monomer in the polyolefin product) on the treated vinylidene chloride copolymer coated substrate; or when other coated polyolefin substrates of any of the same mentioned types of such polyolefins are utilized and are laminated with to support any of such applied polyolefin layers, using any of the other vinylidene chloride copolymer coatings thereon described in the foregoing; or when other polyalkylene imines within the scope indicated in the foregoing specification are employed to provide the adhesion-promoting coating on the surface of the preformed coated polyolefin substrate with which the applied and supported polyolefin layer is laminated.

#### WHAT WE CLAIM IS:—

1. Process for the production of laminated structures which consist of or contain a thermoplastic polymeric substrate to at least one side of which is intimately joined a layer of a non-aromatic hydrocarbon polymer over a thin adhesion-promoting intermediary layer of a polyalkylene imine, in which process the polyolefin is deposited onto the polyalkylene imine modified surface of the preformed thermoplastic polymeric substrate in the form of an extruded molten layer or film.

2. A process in accordance with Claim 1, wherein the non-aromatic hydrocarbon polymer is polyethylene or polypropylene.

3. Process in accordance with Claim 1 of Claim 2, wherein the laminated structures are films or foils.

4. Process in accordance with any one of

Claims 1, 2 or 3 in which the substrate is a film or a foil of a polyester.

5. Process in accordance with Claim 4 in which the polyester is polyethylene terephthalate.

6. Process in accordance with any one of Claims 1, 2 or 3 in which the substrate is a film or foil of a cellulose ester for example, cellulose acetate or cellulose propionate.

7. Process in accordance with any one of Claims 1, or 2 or 3, in which the substrate is a film or a foil of regenerated cellulose or of a non-magnetic polyolefin, for example polyethylene or polypropylene which has on at least one of its sides, a coat or layer of a vinylidene chloride copolymer, whereby the polyalkylene imine and thereafter the molten non-aromatic hydrocarbon polymer are applied to the vinylidene chloride copolymer coated side of the substrate.

8. Process in accordance with Claim 6, in which the vinylidene chloride copolymer contains at least 80 per cent vinylidene chloride.

9. Process in accordance with any one of Claims 1 to 8, in which the intermediary layer of the polyalkylene imine, which is applied to one of the sides of the substrate, is employed in an amount of between 5 grams and 95 grams of the polyalkylene imine per 100 square metres of the substrate.

10. Process in accordance with Claim 9, in which the intermediary layer of the polyalkylene imine is employed in an amount of between 20 and 50 grams of the polyalkylene imine per 100 square metres of the substrate.

11. Process in accordance with any one of Claims 1 to 10, wherein the alkylene units in the polyalkylene imine have from 2 to 4 carbon atoms.

12. Process in accordance with any one of Claims 1 to 11, wherein the polyalkylene imine is polyethylene imine.

13. Process in accordance with any one of Claims 1 to 12, wherein the polyalkylene imine is water soluble.

14. Process in accordance with any one of Claims 1 to 13, wherein the polyalkylene imine has a viscosity of 100 poises in a 20 per cent aqueous solution at 20° C.

15. Process in accordance with any one of Claims 1 to 14, in which the polyalkylene imine is applied in the form of a dilute solution or dispersion in a volatile solvent.

16. Process in accordance with Claim 15, in which the volatile solvent is completely removed before the molten layer of the non-aromatic hydrocarbon is applied.

17. Process in accordance with Claim 15 or Claim 16, wherein the volatile solvent is a lower aliphatic alcohol.

18. Process in accordance with any one of Claims 1 to 17, in which the temperature of the molten non-aromatic hydrocarbon polymer is at the place where it contacts the

substrate is at least 175° C. but beneath the decomposition temperature of the non-aromatic hydrocarbon polymer.

- 5 19. Process for the production of improved laminates by depositing a polyolefin in form of a molten layer onto a polyalkylene imine modified surface of a polymeric substrate substantially as hereinbefore described.

20. Laminated structures whenever pro-

duced by a process as claimed in any one of Claims 1 to 19. 10

21. Laminated structures as claimed in Claim 20 and substantially as described in the specific examples.

BOULT, WADE & TENNANT,  
Chartered Patent Agents,  
111 & 112, Hatton Garden, London, E.C.1,  
Agents for the Applicants.

